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Vapor Phase Isomerization of o-Carborane

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BRIEF

An improved process for the conversion of o-carborane to its meta and para isomers involves heating carborane vapors, admixed with an inert carrier gas in a heated tube at atmospheric pressure. This process accomplishes the isomerization rapidly in a continuous fashion, eliminating the need for the heavy pressure equipment required in previous methods. Optimum conversion of ortho to meta carborane occurred at a tube temperature of 600°C., with a residence time of 0.30 to 0.48 minute and mass flows of 0.73 to 2.98 grams per minute; the meta isomer was recovered in yields up to 98%. Mixtures of meta and para isomers were formed at 700°, the yield of para isomer being about 22% under optimum conditions.

Vapor Phase Isomerization of o-Carborane

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The field of boron chemistry, especially the reactions of organoboron derivatives, has undergone a rapid expansion during the past decade. In the past few years, a new family of unique organoboron compounds have been discovered and investigated. These are evolved from the pyrolysis of diborane to decaborane [14] (20), followed by subsequent reaction of the decaborane with alkynes such as acetylene itself in basic solvents. The organoboron compounds from this type of reaction are known as carboranes and their preparation and chemical properties have been discussed in a number of papers (1,3,4,5,6,7,13,14,15,21,22,24).

Recent work has shown that boron containing polymers, based upon monomeric carborane derivatives, possess outstanding advantages in the formulation of heat resistant materials (2,10,11,12,18,19,17). This has led to further development and evaluation of these materials, with a corresponding requirement for increased amounts of the parent carboranes, especially meta-carborane.

The first member of the $B_{10}C_2H_{12}$ family of carboranes to be discovered and prepared in quantity was the ortho isomer, 1,2-Dicarbadoodecaborane [12] (4,14). Somewhat later, the meta isomer, 1,7-Dicarbadoodecaborane [12], was prepared by thermal rearrangement of the ortho isomer (8,9,25) in a sealed system. Extensions of this technique resulted in the formation of the

para isomer, 1,12-Dicarbadoecaborane [12] (16). The structures assigned to the three isomers are shown in Figure 1 (16,23,26).

The conversion of the ortho to the meta isomer has become of more importance as uses for the meta isomer have increased. The original method for this conversion involved the batch rearrangement of o-carborane, in an autoclave at a temperature of 470° to 480°C, with conversion times ranging from 2 to 48 hours. Batch sizes were necessarily small (approximately 110 to 125 grams) and an extended cooling time was required before the container was safe to open. Yields were high (>90%) and conversion was complete, but the method was slow and cumbersome. Pressures on the order of 200 to 300 p.s.i.g. were usually developed in the chamber during the heating. At 600° to 615°C., a mixture of meta and para isomers resulted. These processes, therefore, were hardly adaptable to the development of a reasonable commercial process.

Since the carboranes sublime readily upon heating, it seemed feasible to attempt the isomerization at atmospheric pressure, subliming the ortho carborane through a heated tube with or without an inert carrier gas and collecting the isomer as a sublimate. A process of this type would, if successful, eliminate the use of heavy pressure equipment and the time lost in lengthy heating and cooling periods during autoclave operations.

EXPERIMENTAL

A sketch of the apparatus, giving an essentially continuous isomerization, is shown in Figure 2. The isomerization tube was Vycor glass, about 30 inches long and 1 inch inside diameter. This was heated with two tube furnaces in series. Tube temperatures were measured by two Chromel-Alumel thermocouples, placed in close contact with the outer tube wall at the center of each furnace.

The o-carborane vaporizer was a cylindrical borosilicate glass cylinder, about 600-ml. volume, heated by an external wrapping of electrical resistance wire. The bottom of the vaporizer was closed by a coarse fritted glass disk, to allow the admission of heated nitrogen as a carrier gas. This nitrogen was pre-heated in a borosilicate glass tube, 1 inch in diameter and 12 inches long, packed with ceramic saddles and heated with electrical resistance tape. Nitrogen flow was measured by rotameter.

After passing through the hot tube, the vaporized isomer proceeded directly to a large borosilicate glass condenser (approximately 4-liter capacity), in which the sublimate was collected and withdrawn as required. The carrier gas then passed through a small water cooled secondary condenser and from this through an oil filled safety trap.

For operation, the tube temperature was brought up to 600°C. and the tube and attached sublimation condenser were purged with nitrogen for 5 to 10 minutes. The vaporizer was charged with up to 400 grams of o-carborane and purged for a few minutes with nitrogen, then attached to the isomerization tube. The vaporizer and nitrogen preheater were heated to 150° to 200°C. and a measured stream of nitrogen passed in. Vapors of sublimate appeared in the condenser within 5 to 10 minutes and continued as long as ortho carborane was being vaporized. Usually, about 80 to 90 minutes was sufficient to vaporize a 250 gram charge of o-carborane. The sublimed meta isomer collected in the bottom of the condenser, and was removed at the end of the run. Purity of product was determined by infrared spectroscopy or vapor phase chromatography.

The first series of experiments were made with small amounts of materials, using carborane vaporizers and condensers of reduced capacity. The Vycor tube was packed with 1/4 inch ceramic saddles

to give better heat transfer to the carborane vapors. In later experiments, the tube was used without packing and much larger amounts of material were isomerized.

Appreciable amounts of p-carborane isomer were made in this apparatus by vaporizing small amounts of ortho carborane through the packed tube, heated to 700°C. The sublimate was a mixture of meta and para isomers, with the percentage of para isomer varying from 35 to 45%. Pure p-carborane was separated from this mixture by vapor phase chromatography (16).

DISCUSSION

A. Ortho-meta isomerization

The possible molecular rearrangements during isomerization have been discussed (9,16). With the type of equipment investigated (1-inch tube with 26-inch heated zone), 550°C. is the lowest temperature at which complete isomerization is observed. Using a packed tube, a residence time of 0.20 minute appears to be necessary at this temperature, as shown by incomplete conversion when residence time was 0.10, 0.11 minute (Table I, Expts. 1 and 2). The yields shown in the tables are based on the amount of m-carborane recovered, and discrepancies in values are only due to purity of the o-carborane used and technique with which the material was recovered. The use of a packed tube, however, presented operating difficulties when a considerable amount of material was isomerized, due to the build up of nonvolatile product from the pyrolysis of impurities in the o-carborane. The problem was eliminated by using the same tube without packing, operating at higher temperature, to compensate for the lower efficiency in heat transfer. A temperature of 600°C. seemed to be the optimum for complete isomerization of o- to m-carborane. The apparatus designed was found most efficient, using a mass flow

of o-carborane of about 3.0 grams per minute with a residence time of about 0.5 minute. As indicated in Table I, other conditions can be used but they are not as convenient.

Since the isomerization is endothermic, one would expect that with greater mass flow, larger residence time and/or higher temperature would be required, and this was observed in practice.

The results demonstrate the advantage of this method of isomerization over that in a closed bomb, both in speed and ease of operation. In addition, we have found that less pure o-carborane can be isomerized in the hot tube, that can be safely tolerated in a closed system. Previous experience in these laboratories has shown that when the purity of o-carborane to be isomerized in an autoclave is below 98%, abnormal pressure build up is experienced which causes leaks and ruptures; in addition, a general degradation of the product is promoted. The ability to use the less pure o-carborane in the flow system allows us to eliminate one more tedious purification step previously required for its preparation.

It should be emphasized that these isomerizations be carried out under an inert gas, free of oxygen. Carborane vapors, at elevated temperatures, will burn upon contact with air and may explode, depending on the concentration of vapor and the amount of oxygen present.

B. Ortho-para isomerization

No p-carborane is detected in these isomerizations until a reaction temperature of 650°C. is reached; the para isomer then is found as about 30% of the volatile reaction products. Some-

what larger proportions of p-carborane are formed at 700°, reaching 45% at a residence time of 0.53 minute. A considerable amount of side reaction is apparent at this temperature, resulting in corrected yields of p-carborane of only 22% (Table II) under the best conditions. This is also true of autoclave isomerization. In these experiments, the isomer composition of the product was estimated from infrared spectra by comparing the relative heights of the characteristic para isomer peak at 9.2 microns with that of the meta isomer peak at 9.8 microns. Infrared spectra for the three isomers have been published (9, 16). The meta and para isomers sublime together when heated, but are easily separated by vapor partition chromatography (16).

CONCLUSIONS

These experiments demonstrate the superiority of hot tube isomerization as compared to that carried out in a closed system. Equipment manipulation is much easier and an isomer production rate of four or five times that of the closed system can be achieved without difficulty. The mechanical development of a power-driven vaporizer, working with a continuous feed of o-carborane, and a cyclone type of sublimate condenser, would permit extended operation of this process. The flow system can isomerize relatively impure carborane without difficulty, as compared with the closed system, which requires purified carborane to avoid difficulties during the reaction.

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TABLE I

Isomerization of Ortho to Meta Carborane
(Packed Tube)

Expt. No.	Tube Temp., °C.	Carrier Gas Flow Rate, ml./min.	Reactant Residence Time (a), min.	Mass Flow g./min.	o-Carborane Vaporized, g.	Sublimate, g.	Yield (%) of m-Carborane
1	550	800	0.10	0.31	9.3	8.8	____(b)
2	500	800	0.11	0.27	8.0	7.2	____(c)
3	550	400	0.20	0.12	40.0	36.1	90.3
4	550	400	0.20	0.06	14.7	14.2	96.5

(Open Tube)

5	500	250	1.08	0.95	39.2	36.7	____(d)
6	600	250	0.48	2.89	222.0	202.5	91.3
7	600	250	0.48	2.85	256.0	244.5	95.5
8	600	250	0.48	2.16	125.0	118.2	94.5
9	600	250	0.48	1.84	46.0	40.5	88.2
10	600	250	0.48	1.22	36.7	32.4	88.3
11	600	250	0.48	2.83	350.0	330.0	95.1
12	600	250	0.48	2.78	250.0	235.0	94.0
13	600	250	0.48	2.67	400.0	387.0	96.8
14	600	250	0.48	2.67	400.0	379.0	94.8
15	600	250	0.48	2.67	400.0	382.0	95.5
16	600	250	0.48	2.67	400.0	387.0	96.8
17	600	250	0.48	2.67	400.0	392.0	98.1
18	600	250	0.48	2.67	400.0	385.0	96.2
19	600	400	0.30	0.83	50.0	37.4	74.9
20	600	400	0.30	0.73	22.0	17.0	77.3
21	600	500	0.24	1.63	49.0	43.0	87.8
22	600	500	0.24	2.68	241.0	229.4	____(e)
23	600	600	0.20	0.50	22.5	20.4	90.7
24	600	600	0.20	0.20	10.0	9.2	92.0
25	600	900	0.13	0.29	10.0	9.3	93.0

(a) All residence times corrected for tube temperature.

(b) Mixture containing 57.2% o-Carborane and 42.8% m-Carborane.

(c) Mixture containing 83.9% o-Carborane and 16.1% m-Carborane.

(d) Mixture containing 89% o-Carborane and 11% m-Carborane.

(e) Mixture containing 5% o-Carborane and 95% m-Carborane.

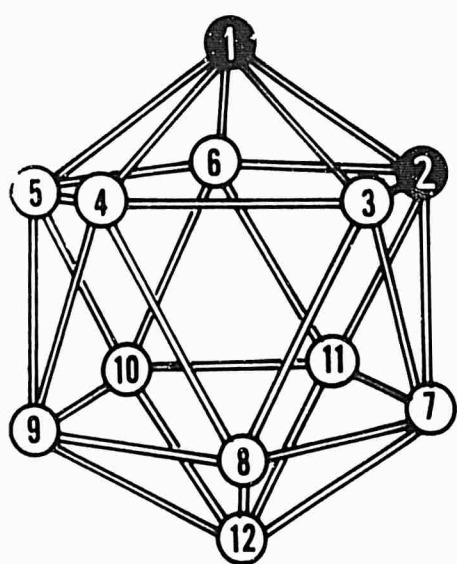
TABLE II

Isomerization of Ortho to Meta and Para Carborane

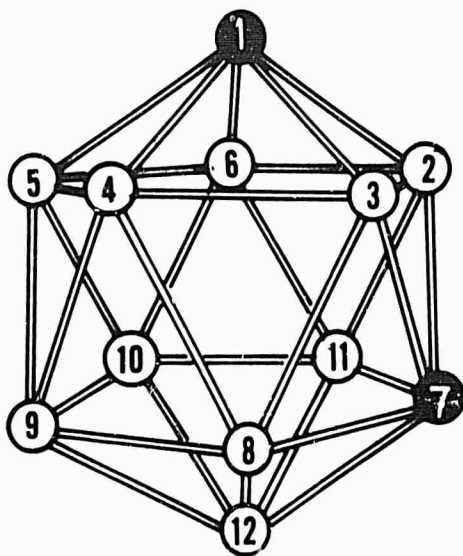
(Packed Tube)

Expt. No.	Tube Temp., °C	Carrier Gas Flow Rate, ml./min.	Reactant Residence Time min.	Mass Flow g./min.	o-Carborane Vaporized, g.	Sublimate g.	Sublimate Composition meta %	para %	Para- Carborane Yield %
1	650	130	0.60	0.05	2.8	1.8	70	30	19
2	700	130	0.53	0.04	2.8	0.8	55	45	12
3	700	200	0.34	0.25	15.0	8.4	60	40	22
4	700	400	0.17	0.09	9.8	5.7	60	40	22
5	700	600	0.11	0.08	4.9	3.2	75	25	16

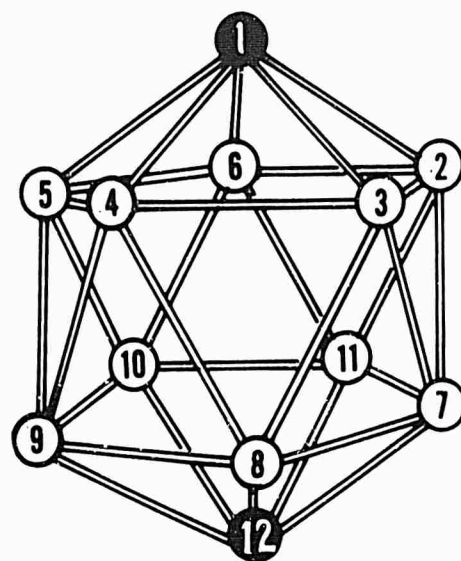
FIGURE 1



ORTHO



META



PARA

In these structures the boron atoms are shown as white circles, with the two carbon atoms in black; hydrogen atoms are omitted for clarity.

Figure 2

Carborane Isomerization Apparatus

Dimensions: Isomerization Tube - "Vycor" Glass, 30" Length, 1" I.D., 35/20 Semi-Ball Joints on Ends.

Carborane Vaporizer - Borosilicate Glass, 9" Overall Ht.; Carborane Chamber, 4" I.D., 4 1/4" Ht. Electrically Heated with a Winding of #22 Nichrome Resistance Wire.

Preheater Tube - Borosilicate Glass, 12" Length, 1" I.D., Electrically Heated with Resistance Tape.

Sublimate Condenser - Borosilicate Glass with Ground Flat Ring Seal. Overall Ht. 18", 6" I.D. Cleaning Rod of 3/8" Diam., 26-28" Overall Length. Rubber Tips on Lower Ends for Sublimate Removal during Operation.

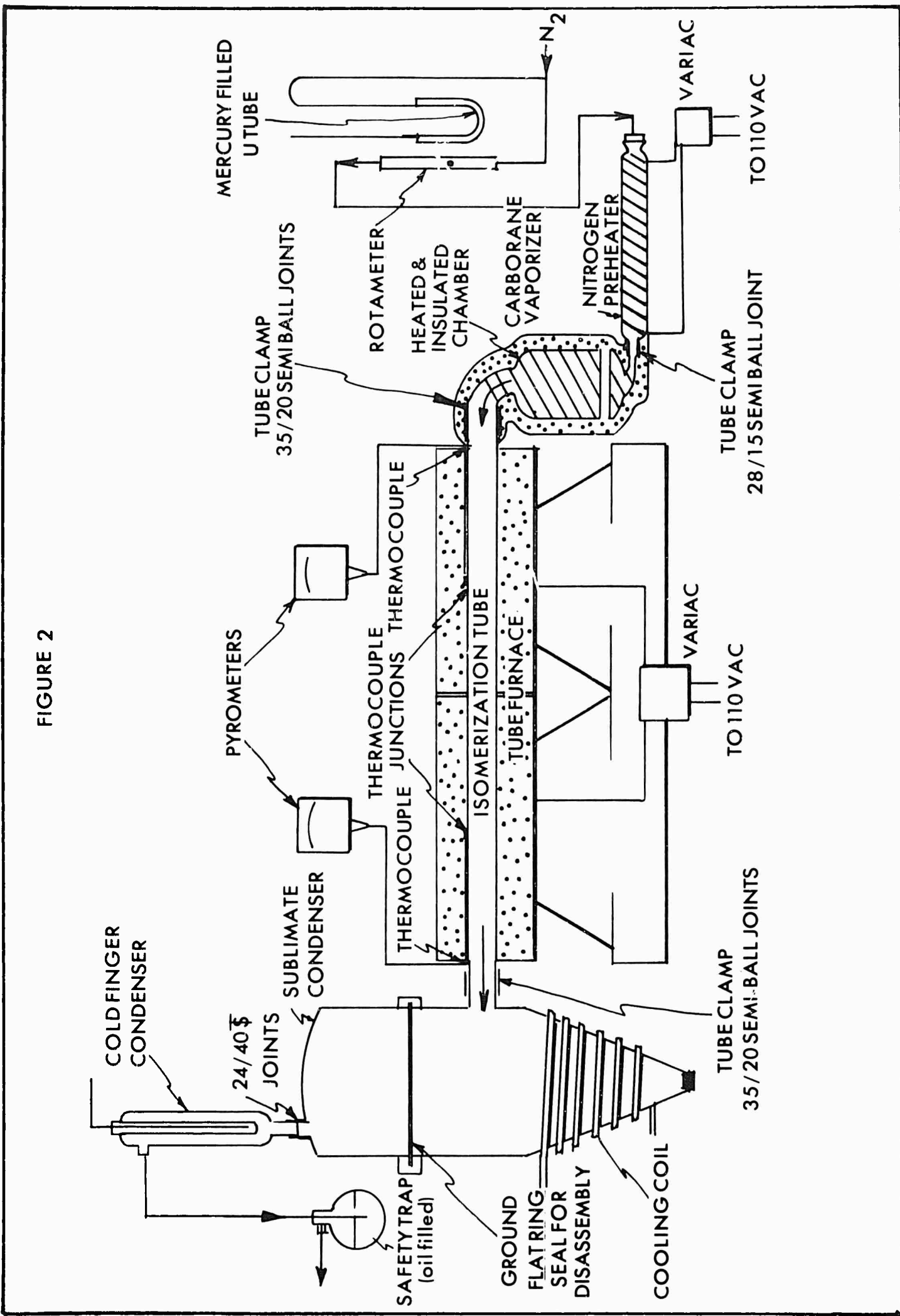


FIGURE 2

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